

PREPARATION AND CHARACTERIZATION OF  
ENVIRONMENTALLY FRIENDLY POLYMERIC BLENDS USING  
SYNTHETIC AND NATURAL POLYMERS

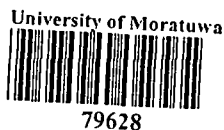
by

G. M. Gayani Dhammika Dias



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This Thesis was submitted to Department of Chemical and Process Engineering of the  
University of Moratuwa in partial fulfillment of the requirement for the Degree of  
Master of Science in Polymer Technology



Department of Chemical and Process Engineering

University of Moratuwa

Sri Lanka

February 02, 2004

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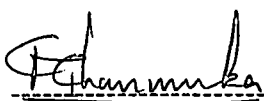
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## DECLARATION

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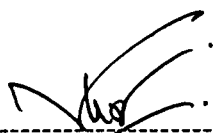
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(Dr. B A J K Premachandra)

## **ABSTRACT**

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This thesis is consisted of four chapters. Chapter one contains an introductory part including scope and the objectives of the research. Since the present research is divided in to three major parts, chapter two, three and four is arranged accordingly. Each chapter includes an introduction discussing the relevant literature, the experimental work, results and discussions and finally, the conclusions drawn. The contents of this thesis can be best summarized as follows.

### **Mechanical properties and biodegradability of composites of LDPE with tapioca starch**

A series of LDPE/starch composites containing different amounts of starch (as wt %) were prepared using tapioca starch in its native granular form. Mixing was done by dissolving LDPE in cyclohexane pre-heated to its boiling point and subsequently dispersing starch granules by using Silverson emulsifier. The composites were studied by using Fourier Transform Infra-red spectroscopy (FTIR). The failure modes, mechanical properties, water absorption, biodegradation and the biodegradation after thermal incubation were investigated as a function of the composition of the composite. It was found that the incorporation of starch into LDPE matrix has reduced the ductility of the composite. The mechanical properties of the composites, especially the tensile strength and elongation at break were significantly low compared to those of neat LDPE. A significant improvement in modulus was shown by the composites. It was found that the mechanical properties were depended on the composition of the composite.

The extent of the biodegradability, after exposure to  $\alpha$ -amylase enzyme solution, was assessed by weight loss measurements and loss of mechanical properties such as tensile strength and percentage elongation. It was found that these composites are biodegradable and the rate of biodegradation increases with increasing starch content. The extent of biodegradation after thermal incubation was assessed by the loss of tensile strength measurements of the composites after incubation of the samples in an

air circulation oven at 70 °C and subsequently exposing to  $\alpha$ -amylase enzyme solution. It was found that the degradability of the samples was not significantly affected by the thermal incubation.

#### **Preparation and characterization of long chain fatty acid esters of tapioca starch**


A series of starch esters with different degree of substitution (DS) were prepared and studied. The esters were prepared by acylation of tapioca starch with appropriate acid chlorides such as stearoyl and oleoyl chlorides. Fourier transform infrared (FTIR) spectroscopy confirmed the formation of the starch esters and their DS. As a measurement of the DS of an ester the peak height ratio responsible for O-H bond stretching to C=O bond stretching of the esters were considered. The DS of starch stearates were 5.3, 4.5, 2.6, 2.0 and 1.60. The DS of starch oleates were 3.55, 2.0, 1.90 and 1.21. With increasing DS the color intensities of the esters were improved. Melting temperatures of the esters were determined by using Differential thermal analyzer. The thermo-oxidation degradation of tapioca starch and starch esters, were assessed by using Fourier Transform Infra-red (FTIR) spectroscopy, after the incubation of the samples in an air circulation oven at 70 °C. The presence of thermo-oxidative degradation was shown in both types of the starch esters. Starch has not shown thermo-oxidative degradation.

#### **Mechanical properties and biodegradability of composites of LDPE with fatty acid esters of tapioca starch**

A series of Low Density Polyethylene (LDPE) composites containing different amounts of fatty esters of starch were prepared. Mixing was done by dissolving LDPE, in cyclohexane pre-heated to its boiling temperature, and subsequently, mixing starch esters using Siverson Emulsifier. Two different types of starch esters, starch stearate and oleate with different (DS) were utilized in the preparation of these LDPE composites. Polarized light micrographs were used to assess the miscibility of LDPE with starch esters.

The miscibility of the components was found to be improved with increasing DS of the ester. Water absorption, mechanical properties, biodegradation and biodegradation after thermal incubation were investigated as a function of the composition of the composite. Comparing with the LDPE/starch composites a significant reduction in the water absorption was resulted in the LDPE/starch ester composites. It was found that as the amount of esters increases in the composite, the tensile strength and especially the elongation at break decrease non-linearly. The LDPE/starch ester composites containing starch esters of high DS have shown improved tensile properties than those of LDPE/starch composites. As expected, the fatty ester chains in the starch ester molecules have not shown the plasticizing effect in the composite. The percentage elongation properties were significantly reduced with the introduction of the esters into LDPE.

The extent of the biodegradability of the composites after exposure to  $\alpha$ -amylase and lipase enzyme solutions was assessed by weight loss and mechanical properties measurements. The rate of biodegradation of LDPE/starch ester composites was relatively low compared to that of LDPE/starch composites. The rate of biodegradation of these LDPE/starch ester composites further decreases with increasing DS of the ester in the composite. The extent of the biodegradation of the composites after incubation of the samples at air circulation oven at 70 °C and subsequently immersing in the enzymatic solutions was assessed by the tensile strength measurements. It was found that the degradability of the ester composites was significantly high and the degradation rate increases with the increasing DS of the ester. Highest rate of degradation was observed in the LDPE/starch ester composite containing starch oleate of the highest DS.

To my parents,  
the first teachers in my life,  
To my husband,  
for his motivation towards the success in my life,  
To my son,  
whose smile gave me a new hope to my life,  
I dedicated this thesis,  
with joy and happiness,  
 to owe my gratitude to them.

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Without them, their love and blessing, I may not finish this thesis today.

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## **TABLE OF CONTENTS**

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	<b>Page No.</b>
<b>Declaration</b>	<b>i</b>
<b>Abstract</b>	<b>ii</b>
<b>Acknowledgements</b>	<b>v</b>
<b>Table of contents</b>	<b>viii</b>
<b>List of Tables</b>	<b>xii</b>
<b>List of Figures</b>	<b>xiii</b>
<b>List of Abbreviations</b>	<b>xvi</b>

### **CHAPTER ONE – INTRODUCTION**

1.1. Background motivation	2
1.2. Objectives	5

### **CHAPTER TWO – STRUCTURE, MECHANICAL PROPERTIES AND BIODEGRADABILITY OF COMPOSITES OF LDPE WITH TAPIOCA STARCH**

<b>2.1.INTRODUCTION</b>	<b>7</b>
2.1.1. The process of biodegradation	7
2.1.2. Biodegradation of polymers	8
2.1.3. Biodegradable thermoplastic materials	10
2.1.4. Starch	11
2.1.5. Polymeric materials containing starch as a component	14
<b>2.2. Theories on the effect of fillers on the failure modes and mechanical properties of a composite</b>	<b>18</b>
2.2.1. The effect of fillers on the failure modes of a polymeric composite	18
2.2.2. Effect of fillers on extension	18
2.2.3. Effect of fillers in tensile strength of a polymeric composite	19
2.2.4. Effect of fillers in modulus of a composite	20

<b>2.3. EXPERIMENTAL</b>	22
2.3.1. Materials	22
2.3.2. Preparation of LDPE/starch composites	22
2.3.3. FTIR analysis of LDPE/starch composites	22
2.3.4. Analysis of the morphology of LDPE/starch composites	23
2.3.5. Determination of the mechanical properties of the LDPE/starch composites	23
2.3.6. Determination of the water absorptivity of LDPE/starch composites	23
2.3.7. Determination of the biodegradability of LDPE/starch composites	23
2.3.8. Determination of the biodegradability of LDPE/starch composites after thermal incubation	24
<b>2.4 RESULTS AND DISCUSSION</b>	
2.4.1. FTIR spectrometric analysis of LDPE/starch composites	25
2.4.2. Analysis of the morphology of LDPE/starch composites	27
2.4.3. Analysis of the failure modes of LDPE/starch composites	27
2.4.4. Mechanical properties of LDPE/starch composites	31
2.4.5. Water absorptivity of LDPE/starch composites	36
2.4.6. Weight loss of LDPE/starch composites after enzymatic degradation	36
2.4.7. Variation in mechanical properties after enzymatic degradation of LDPE/starch composites	40
<b>2.5. CONCLUSIONS</b>	44
 <b>CHAPTER THREE – PREPARATION CHARACTERIZATION OF LONG CHAIN FATTY ACID ESTERS OF TAPIOCA STARCH</b>	 45
<b>3.1. INTRODUCTION</b>	46
<b>3.2. EXPERIMENTAL</b>	49
3.2.1. Materials	49
3.2.2. Preparation and purification of starch esters	49
3.2.3. FTIR spectrometric analysis of starch esters	50
3.2.4. Determination of the melting temperatures of starch esters	50

3.2.5. Determination of thermo-oxidative degradation of starch esters	50
<b>3.3. RESULTS AND DISCUSSION</b>	<b>51</b>
3.3.1. FTIR spectrometric analysis of starch esters	51
3.3.2. Thermal analysis of starch esters	58
3.3.3. Analysis of thermo-oxidative degradation of starch esters	60
<b>3.4 CONCLUSIONS</b>	<b>65</b>
 <b>CHAPTER FOUR – STRUCTURE, MECHANICAL PROPERTIES AND BIODEGRADABILITY OF COMPOSITES OF LDPE AND FATTY ACID ESTERS OF TAPIOCA STARCH</b>	 <b>66</b>
<b>4.1 INTRODUCTION</b>	<b>67</b>
<b>4.2 EXPERIMENTAL</b>	<b>73</b>
4.2.1. Materials	73
4.2.2. Preparation of LDPE/starch ester composites	73
4.2.3. Characterization of LDPE/starch ester composites	73
<b>4.3. RESULTS AND DIASCUSSION</b>	<b>75</b>
4.3.1. FTIR spectral analysis of LDPE/starch ester composites	75
4.3.2. Analysis of the morphology of LDPE/starch ester composites	75
4.3.3. Analysis of the failure modes of LDPE/starch ester composites	78
4.3.4. Determination of the mechanical properties of LDPE/starch ester composites	86
4.3.5. Analysis of water absorptivity of LDPE/starch ester composites	95
4.3.6. Analysis of the biodegradation of LDPE/starch ester composites	98
4.3.7. Determination of the Biodegradability and thermo-oxidative degradability of LDPE/starch ester composites	104
<b>4.4 CONCLUSIONS</b>	<b>108</b>

<b>CHAPTER FIVE</b>	109
<b>5.1. FUTURE WORK</b>	110
<b>5.2. LIST OF REFERENCES</b>	111



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## **LIST OF TABLES**

---

	<b>Page No.</b>
<b>Table 2.1.</b> Infrared Vibrations and Assignments for PE and PES composites	25
<b>Table 2.2.</b> Mechanical properties of PES composites	31
<b>Table 3.1.</b> Infrared Vibrations and Assignments of starch, starch esters, fatty acids and acid anhydrides	51
<b>Table 3.2.</b> Degree of substitution and the appearance of the starch esters	55
<b>Table 4.1.</b> Mechanical properties of LDPE/starch ester composites	87
<b>Table 4.2.</b> Mechanical properties of LDPE/starch ester composites after enzymatic degradation	101
<b>Table 4.3.</b> Tensile strength properties of LDPE/starch ester composites after thermo-oxidative and subsequent enzymatic degradation	106



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## LIST OF FIGURES

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	Page No.
<b>Figure 1.0.</b> Schematic representation of amylose	12
<b>Figure 2.0.</b> Schematic representation of amylopectin	13
<b>Figure 2.1.</b> FTIR spectra of (a) PE and composites of (b) PES-5 (c) PES-15 and (d) PES-25	26
<b>Figure 2.2.</b> Polarized light micrographs of LDPE and LDPE/starch composites containing different amounts of starch	28
<b>Figure 2.3</b> Stress strain curves for (■) PE, (●) PES-5, (▲) PES-15 and (—) PES-25 composites	30
<b>Figure 2.4 (a).</b> Variation in the tensile strengths as a function of the starch content	32
<b>Figure 2.4 (b).</b> Variation in % Elongation at break as a function of the starch content	34
<b>Figure 2.4 (c).</b> Young's Modulus as a function of the starch content	35
<b>Figure 2.5.</b> Percentage weight change of (■) PES-5, (●) PES-15 and (▲) PES-25 composites during immersion in water	37
<b>Figure 2.6.</b> Weight loss of PES samples after enzymatic degradation	39
<b>Figure 2.7 (a).</b> Variation in tensile strength of PE and PES samples (■) before the degradation, (●) after enzymatic degradation (▲) enzymatic degradation after thermal incubation	41
<b>Figure 2.7 (b).</b> Variation in % elongation of PE and PES samples (■) before the degradation, (●) after enzymatic degradation and (▲) enzymatic degradation after thermal incubation	42
<b>Figure 3.1.</b> FTIR spectra of (a) tapioca starch and (b) starch stearate	53
<b>Figure 3.2.</b> FTIR spectra of (a) starch stearate and (b) starch oleate	54
<b>Figure 3.3.</b> FTIR spectra of starch stearates with different DS	56
<b>Figure 3.4.</b> FTIR spectra of starch oleates with different DS	57
<b>Figure 3.5.</b> Thermogram of a starch oleate	59

<b>Figure 3.6.</b> FTIR spectra of starch oleate (a) before and (b) after thermal incubation	61
<b>Figure 3.7.</b> FTIR spectra of starch stearate (a) before and (b) after thermal incubation	62
<b>Figure 3.8.</b> FTIR spectra of starch (a) before and (b) after thermal incubation	64
<b>Figure 4.0.</b> The biodegradation mechanism of polyethylene	71
<b>Figure 4.1.</b> FTIR spectra (a) LDPE, LDPE/starch and LDPE/starch stearate composite	76
<b>Figure 4.2 (a).</b> Polarized light micrographs of PESS composites	77
<b>Figure 4.2 (b).</b> Polarized light micrographs of PESO composites	79
<b>Figure 4.3 (a).</b> Stress-strain curves for PESS 5.3 composites containing starch tearate of (■) 5, (●) 15 and (▲) 25 wt %	80
<b>Figure 4.3 (b).</b> Stress-strain curves for PESS 2.6 composites containing starch stearate of (■) 5, (●) 15 and (▲) 25 wt %	81
<b>Figure 4.3 (c).</b> Stress-strain curves for PESS 1.6 composites containing starch stearate of (■) 5, (●) 15 and (▲) 25 wt %	82
<b>Figure 4.4 (a).</b> Stress-strain curves for PESO 3.55 composites containing starch oleate of (■) 5, (●) 15 and (▲) 25 wt %	83
<b>Figure 4.4 (b).</b> Stress-strain curves for PESO 2.0 composites containing starch oleate of (■) 5, (●) 15 and (▲) 25 wt %	84
<b>Figure 4.4 (c).</b> Stress-strain curves for PESO 1.21 composites containing starch oleate of (■) 5, (●) 15 and (▲) 25 wt %	85
<b>Figure 4.5 (a).</b> Variation in tensile strength of (●) PESS- 5.3, (▲) PESS- 2.6, (Δ) PESS-1.6 and (■) PES samples	88
<b>Figure 4.5 (b).</b> Variation in tensile strength of (●) PESO-3.55, (▲) PESO- 2.0, (Δ) PESO- 1.21 and (■) PES samples	89
<b>Figure 4.5 (c).</b> Percentage reduction of tensile strengths vs composition of the composites of (■) PES, (●) PESS 5.3, (▲) PESS 2.6, (Δ) PESS 1.6, (□) PESO 3.55, (*) PESO 2.0 and (○) PESO 1.21.	91
<b>Figure 4.6 (a).</b> Variation in % Elongation at break with the starch/starch ester content of (■) PES, (▲) PESS-5.3, (□) PESS 2.6, and (▨) PES 1.6 samples	93
<b>Figure 4.6 (b).</b> Variation in % Elongation at break with the starch/starch ester	94

content of (▨) PES, (▧) PESO-3.55, (□) PESO-2.0, and (▩) PESO-1.21 samples

**Figure 4.7 (a).** Percentage weight change of (■) PESS 2.6-5, (●) PESS 2.6-15 and (▲) PESS 2.6-25 composites during immersion in water 96

**Figure 4.7 (b)** Percentage weight change of (■) PES-15, (●) PESS 2.6-15, (x) PESO 3.55-15 and (▲) PESS 5.3-15 composites during immersion in water 97

**Figure 4.8.** % Weight loss during enzymatic degradation of (▨) PES, (▧) PESS-2.6, (□) PESO 3.55, and (▩) PESS 5.3 samples 99

**Figure 4.9 (a).** % Reduction in tensile strength after enzymatic degradation of (■) PES, (▲) PESS 2.6, (Δ) PESS 2.6 and (●) PESS 5.3 samples 102

**Figure 4.9 (b).** % Reduction in elongation at break after enzymatic degradation of (■) PES, (▲) PESS 2.6, (Δ) PESS 2.6 and (●) PESS 5.3 samples 103

**Figure 4.10.** % Reduction in tensile strength after thermo-oxidative and enzymatic degradation of (▲) PESO 3,55, (■) PESS 3.55 and (●) PESS 2.6 samples 107





## LIST OF ABBREVIATIONS

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CaCO <sub>3</sub>	- Calcium Carbonate
DS	- Degree of Substitution
EAA	- Ethylene Acrylic Acid
EVOH	- Ethylene Vinyl Alcohol
FTIR	- Fourier Transform Infra- Red
h	- Hours
HCl	- Hydro Chloric Acid
HDPE	- High Density Polyethylene
LDPE/PE	- Low Density Polyethylene
MPa	- Mega Pascal
PCL	- Poly Caprolactone
PET	- Polyethylene Terephthalate
PES	- Low Density Polyethylene/ Starch Composite
PESO	- LDPE/ Starch Oleate Composite
PESS	- LDPE/ Starch Stearate Composite
PG	- Poly Glycolide
PHB	- Poly Beta hydroxy Butyrate
PHV	- Poly Hydroxy Valarate
PL	- Poly Lactic
rpm	- Rounds per minutes
TiO <sub>2</sub>	- Titanium dioxide
T <sub>m</sub>	- Melting temperature
T <sub>g</sub>	- Glass transition temperature
wt %	- Weight percentage